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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No.

EL696834535US

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TITLE OF THE INVENTION (500 characters max)		
METHOD FOR SCALE REMOVAL		

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ENCLOSED APPLICATION PARTS (check all that apply)			
<input checked="" type="checkbox"/> Specification	Number of Pages	16	<input type="checkbox"/> CD(s), Number
<input type="checkbox"/> Drawing(s)	Number of Sheets		<input type="checkbox"/> Other (specify)
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76			
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT			
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.		FILING FEE AMOUNT (\$)	
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Respectfully submitted,

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06/17/2002

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31,278

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This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

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J1040 U.S. PTO
60/417064
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Our File No.: IN-10015

Re: METHOD FOR SCALE REMOVAL

Assistant Commissioner for Patents
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METHOD FOR SCALE REMOVAL

[0001] This invention relates to a method for removing scale from heat exchangers, evaporators, heaters or other equipment that has problems with scale formation.

[0002] As an example, one step in the manufacture of raw sugar is the concentration of the juice expressed from sugar cane following clarification. The juice is expressed in a mill tandem or diffuser and then clarified with milk of lime and heating to above the boiling point, flocculent addition and settling/separation of the muds or impurities in a clarifier. The heating of the cane juice is typically accomplished in shell and tube or plate heat exchangers. These heat exchangers foul after several days of operation and require cleaning. The clarified juice is concentrated in multiple effect evaporators of the standard or calendria type or falling or rising film plate types. During evaporation, scale forms in the evaporator bodies, severely reducing heat transfer and cleaning is required approximately every one to two weeks. The type of scale that is formed is a function of the cane variety used, weather and soil conditions during the growth of the cane, the sugar and thus nonsugar expression yield, and process conditions as liming, time=temperature relationships during clarification, concentration, etc.

[0003] The clarified juice at some 15% sucrose is concentrated to a syrup of approximately 60 – 66% sucrose. The syrup is processed into raw sugar (A and B sugars) and C-sugar. The latter is used internally as seed for the A and B strikes in the standard boiling scheme. Other boiling schemes are in use as well and the sugar boiling may be done in batch or continuous pans. In all cases the vacuum pans used will show scale forming and require periodic cleaning. Scaling is the deposition of non-sugar materials that become insoluble in the juice solution as it becomes more concentrated and exceeds the solubility products of the compounds

in question. Scaling in the evaporator bodies, especially the first and last one typically can be very severe. The scale in the last body is especially difficult to remove. The scale has a low thermal conductivity and its accumulation on the heat exchanger surfaces reduces the efficiency and productivity of the sugar factory considerably.

[0004] Because of the formation of scale, evaporator bodies are cleaned about every 10-15 days. Typically they are cleaned with caustic soda and sometimes some soda ash, and with acid. A common practice is to boil for several hours with dilute aqueous alkaline solution, a water wash followed by an acid boil. An additional step using materials such as fluorides or gluconic acid can be used to attack silicates and leave the tubes spotlessly clean. Because of the cleaning cycle used, the production of concentrated juice is interrupted for about 10 to 14 hours.

[0005] The major scale components are typically: silicon, calcium, magnesium and phosphorus. In some parts of the world the scale may be high in iron and aluminum as well.

[0006] It has also been found that some scale, such as that comprising calcium oxalate, calcium magnesium aconitate, and crystalline silica is not readily attacked by either dilute acid or caustic. Accordingly, there remains a need for additional agents and methods that can be used to remove scale from sugar factory evaporator vessels more efficiently and more rapidly. The cost of the cleaning materials and the downtime and ensuing loss of production are significant.

[0007] This invention relates to a means of removing scale from evaporator vessels rapidly, efficiently, economically and with minimal corrosion.

[0008] More particularly, this invention relates to a means of removing scale in a cost effective and less time consuming manner, thus increasing the productivity of the sugar factory.

[0009] In one embodiment, this invention relates to a general method for the removal of scale from sugar evaporators.

[00010] In another embodiment of the invention, this invention relates to a method of removing hard scale, typically found in the last evaporator body tubes of an evaporator.

[00011] The invention relates to a method for removing the scale from equipment having scale build-up such as heat exchangers, evaporators, heaters or other equipment which comprises treating the evaporator surfaces having scale with a solution of a sodium salt of a chelating agent such as ethylenediaminetetraacetic acid or diethylenetriamine-pentaacetic acid, for example, tetrasodium ethylenediaminetetraacetic acid or pentasodium diethylenetriamine-pentaacetic acid.

[00012] In another embodiment the invention relates to a method for removing scale from equipment having scale build-up such as heat exchangers, evaporators, heaters or other equipment which comprises treating the evaporator surface having scale with a solution of a sodium salt of a chelating agent such as tetrasodium ethylenediaminetetraacetic acid or pentasodium diethylenetriamine-pentaacetic acid in combination with caustic and at least one of an additional compound effective in removing hard scale such as a fluoride, gluconic acid or sodium acid sulfate.

[00013] It is also contemplated that the method of this invention can be used to clean any evaporator for any industry where there are evaporators that develop scale containing one or more of the components of the scale formed in sugar factory evaporators.

[00014] The present invention may be understood more readily by reference to the following detailed description of exemplary embodiments of the invention and the examples included therein.

[00015] In this specification and in the claims that follow, reference will be made to a number of terms that shall be defined to have the following meanings:

[00016] As used throughout, the term "evaporator" is used to mean an apparatus or plant used to concentrate solutions of organic (or inorganic) compounds such as sugar or other naturally occurring water-soluble products where the evaporation causes the buildup of scale within the apparatus or plant. The usual evaporator is a multiple effect evaporator. There are several types of evaporators including those with a steam chest and multiple vertical tubes and those having falling or rising film (plate) evaporators.

[00017] In general, "scale" means the deposit of materials whose solubilities progressively decrease with increasing concentration. These insoluble impurities form a hard deposit within the evaporator body. The composition of the scale varies between evaporator vessels, the product being obtained, the place where the plant that yielded the organic or inorganic extract grew and the time during the growing season of the plant that the product was extracted. Non-limiting examples of the impurities obtained include calcium phosphate, calcium carbonate, silicic acid, calcium silicates, calcium oxalates; iron and aluminum silicates, calcium oxalate, calcium- or silica-containing minerals such as amorphous calcium phosphate, Whitlockite, Brushite, Collensite, Hydroxyapatite, Okenite, Calcium silicate hydroxide, Whewellite, Weddellite, Calcite, Gypsum, Magnesium carbonate, Babingtonite, Carbonate-fluorapatite, Amorphous Silica, alpha-quartz (crystalline) calcium magnesium aconitate, calcium aconitate, resenhahnite, and Maghemite; proteins, amino acids, waxes and lipids, cellulose and hemi-cellulose. The first bodies of an evaporator typically contain calcium phosphate, calcium carbonate and organic matter while the latter one(s) contain silica, calcium silicates, iron and aluminum

silicate, calcium oxalate, calcium aconitate, dicalcium-magnesium aconitate along with calcium phosphate, sulfate and carbonate and organic matter. The scale in the last body is typically the thickest, as well as the hardest and the most difficult to remove. Scale also does not deposit evenly on tubes and it is typically thicker at the bottom where circulation is slow.

[00018] "Fluoride" refers to fluoride ions that are added to the cleaning solution in the form of a salt such as ammonium bifluoride, KBF_4 (potassiumfluoborate), sodiumfluoborate, fluosulfonic acid or sodium fluoride. It has been found that fluoride can be added to help in the removal of the hard scale, typically found in the last tube(s).

[00019] The preferred cleaning solutions of the invention are solutions of chelates, preferably sodium salts of polycarboxylic acids such as tetrasodium ethylenediaminetetraacetic acid and pentasodium diethylenetriamine-pentaacetic acid. Concentrated formulations of these compounds are commercially available. In actual use the solutions are diluted to a concentration of from about 3 to about 100 g/L, preferably from about 25 to about 75 g/L, most preferably from about 55 to about 70 g/L.

[00020] The pH of the chelate solution is about 7 to about 12, preferably about 9.0-10.0. In the event the pH of the solution is not high enough, particularly when fluoride has been added, sodium hydroxide is added to maintain the pH.

[00021] The temperature of the solution during the cleaning process is generally between about 20°C and about 120°C, preferably between about 50°C and about 110°C, most preferably about 100°C to about 102°C.

[00022] In a typical cleaning procedure, water is added to a mixing tank. The concentrated chelate solution with appropriate additives such as, wetting agents, corrosion inhibitor, etc, and optionally is then added to

the mixing tank and the mixture is pumped into an evaporator to a predetermined level. Steam is applied and the mixture is boiled within the evaporator at atmospheric pressure for a period of approximately 1 – 4 hours, generally about 2 hours), and then removed. After a water rinse, the evaporator is ready for use.

[00023] The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how the compositions and methods claimed herein are made and evaluated, and are intended to be purely exemplary of the invention and are not intended to limit the scope of what the inventors regard as their invention. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.) but some errors and deviations should be accounted for. Unless indicated otherwise, percent is percent by weight given the component and the total weight of the composition, temperature is in °C or is at ambient temperature, and pressure is at or near atmospheric.

[00024] An additional advantage of the method of the instant invention is the reduction of the corrosion that takes place when removing scale by using acid.

Examples

[00025] Six types of chelate-based formulations were tested. Four were in liquid form and two were powders. The chelate-bases formulations were ready for use.

A	Trilon B	Na ₄ EDTA 39% (liquid)
B	Trilon CS	DPTA 98% (powder)
C	Trilon D	Na ₃ HEDTA 40% (liquid)
D	BAD	(NH ₄) ₄ EDTA 40% (liquid)
E	TRILON BS90	90% (EDTA powder)
F	CHEL DTPA	Na ₅ DTPA 40% (liquid)

[00026] Tubes were obtained from four sugar factories. The tubes varied in size and length depending on the body from which they were removed. All the tubes were carefully cut into three sections, top, middle and bottom. The sections were further cut into several smaller sections 1.5 to 1.7 inches long.

Example 1

[00027] The liquid chelate solutions were arbitrarily diluted to 5 g/L. Solubility limitations restricted the quantities of powder formulations to 1.23 to 13 g/L. Pre-weighed tube sections were totally immersed in 400 to 450 ml of the chelate solution and either kept at ambient temperature (24°C) or boiled (102°C) for 6 hours. In some instances the pH of the solution was adjusted with HCl or sodium hydroxide to approximately 7. The effect was not satisfactory necessitating an increase of the concentration of Trilons B, C, D, and BAD to 50 g/L. After treatment, the tubes were gently rinsed with a stream of tap water, allowed to dry and re-weighed. Scale not completely removed by the test solution was removed by gently scrubbing with a scouring pad dipped in dilute HCl and rinsing with water. The clean tubes were dried and re-weighed. Weight differences were used to quantify the amount of scale removed. In

addition the bonding of the residue to the inner surface of the tube was noted.

[00028] Tables I, II and III show data pertaining to this study.

Table I

Distribution of Scale

Vessel	Amount of Scale (g/ft ²)
Heater (Location A)	29.43
Pre-Evaporator (Location B)	14.72
First Effect (Location B)	3.96
Second Effect (Location B)	5.94
Third Effect (Location B)	4.81
Fourth Effect (Location B)	13.30

Table II

Distribution of Scale in the Fourth Effect Tube

Vessel	Amount of Scale (g/ft ²)
Top 2.2 ft	8.49
Mid 2.2 ft	13.30
Bottom 2.2 ft	17.55

Table III

Effect of Treatment with Chelate

Chelate	Quantity (g/L)	PH	Time (hr)	Temp °C	% Reduction
A	5	7.00	6	25	85.1±4.2
A	45	11.5	2	102	92.7±2.3

Chelate	Quantity (g/L)	PH	Time (hr)	Temp °C	% Reduction
B	5	7.00	6	25	25.4±13.7
B	5	7.00	6	102	84.8±8.8
B	50	11.5	2	102	93.0±9.0
C	5	11.5	6	25	37.7±5.4
C	5	7.00	6	102	83.1±2.6
C	50	11.5	2	102	83.2±4.4
D	5	7.00	6	25	54.6±1.9
D	50	7.00	6	102	84.3 ± 1.6
E	1.25	7.00	6	25	41.9±10.5
E	1.25	7.00	6	102	81.1±12.1
F	5	7.00	6	25	82.7±1.6
F	13	2.5	2	102	87.4±3.4

Example 2

[00029] Three formulations showing potential for removing scale were tested with samples from the Fourth Effect (Location B). The testing protocol was the same as used in Example 1. Sections were immersed in 450 ml of 30, 40 or 50 g Na₄EDTA/L of solution at the natural pH of the chelate solution (11.5) and heated for a predetermined period of time. Corrosion was measured by weight depletion of small copper or carbon steel chips placed in the same solution used for scale removal. Treatments of water and of caustic (3%)/acid(5%) were used as controls. The results are set forth in Table IV.

Table IV

Effect of Chelate Treatment

Chelate	Trials	Temp °C	Conc. g/L	Time (hr)	Amount of scale (g)	% Removed
A	5	102	50	2	1.34 ± 0.46	97.15 ± 3.29
A	2	102	50	4	1.23 ± 0.33	98.00 ± 0.36
B	6	102	50	2	1.17 ± 0.45	96.03 ± 5.56
B	2	102	50	4	1.02 ± 0.67	98.19 ± 1.25
C	4	102	50	2	1.24 ± 0.50	84.67 ± 3.14
C	4	102	50	4	1.00 ± 0.32	97.49 ± 0.94
A	6	102	30	2	1.70 ± 0.02	92.39 ± 5.60
A	6	102	40	2	1.28 ± 0.11	97.15 ± 6.99
B	6	102	30	2	1.38 ± 0.37	89.13 ± 9.53
B	6	102	40	2	1.18 ± 0.41	92.88 ± 9.32
A	6	24	50	12	0.88 ± 0.07	90.91 ± 10.93
B	6	24	50	12	0.89 ± 0.11	94.66 ± 7.24
Water						43.7
Caustic/ Acid						98.5

Example 3

[00030] A pilot test was carried out at a sugar factory at Location A. To simulate the laboratory test procedure, each vessel of a triple evaporator set was filled to slightly above the tube sheet level. The estimated working volume of each vessel was 17,104L (4519 gallons). The amount of chelate added was increased one percentage point above

that used in the laboratory. The concentration of Na_4EDTA in the first, second and third bodies was 65.7, 62.9 and 66.2 g/L respectively. Steam was applied and the material let boil at 100°C for two hours at atmospheric pressure.

[00031] After a water rinse, the vessels were visually inspected for residual scale. None was observed.

Example 4

[00032] The corrosive effects of the chelate solution on copper tubes and carbon steel were measured by determining the weight depletion of small copper or carbon steel chips placed in the same solution used for scale removal. The chips were weighed, placed in 450 ml of solution and heated at 102°C for two hours. They were then rinsed and dried and the percent weight loss was measured. Treatments of water and of caustic acid (7%) were used as controls. The results are shown in Tables V and VI.

Table V: Corrosive Effects on Copper Tubes

Chelate	Amount (g)	# of Trials	Orig. Weight (g)	% Wt Loss	% Wt Loss/Hour
A	22.5	19	2.5353	0.0179	0.00895 ± 0.00428
B	22.5	3	2.4549	0.0445	0.02225 ± 0.02915
Water	450	3	7.8142	0.0218	0.01088 ± 0.00518
Acid	7%	6	2.55105	0.81485	0.4242 ± 0.06086

Table VI: Corrosive Effects on Carbon Steel

Chelate	Amount (g)	# of Trials	Orig. Weight (g)	% Wt Loss	% Wt Loss/Hour
A	22.5	6	42.9777	0.00336	0.00168±0.00116
B	22.5	6	40.7152	0.00352	0.00156±0.00135
Water	22.5	6	41.7066	0.00323	0.00162±0.00083

Example 5

[00033] A fourth effect evaporator tube (1.5" ID) section with scale, weighing 31.2296 grams and having an internal surface area of 4.123 square inches was submerged in a solution of 4% w/w Chelate A and 1.25% of sodium acid sulfate. The ratio of cleaning solution to internal tube area was approximately the same as in the sugar factories. The pH of the starting solution was 9.01. The tube section was boiled in the solution at atmospheric pressure for 90 minutes. The tube section was removed, washed with water, dried and weighed. The final pH was 5.97. The tube was totally clean. The scale quantity was 77.2 grams per square foot.

Example 6

[00034] A fourth effect evaporator tube section with scale, weighing 36.5309 grams and having an internal surface area of 5.8095 square inches was submerged in a solution containing 4% w/w Chelate A and 3.6% ammonium bifluoride. The ratio of cleaning solution to internal tube area was approximately the same as used in the sugar factories. The pH of the starting solution was 9.41. The tube section was totally clean after

2 hours of boiling at atmospheric pressure. The scale quantity removed was 64.3 grams per square foot and the final pH was 7.15.

Example 7

[00035] A fourth effect tube section with scale, weighing 82,4566 grams and an internal surface area of 13.1844 square inches was submerged in a solution of 5% w/w EDTA (trilon B) and 2.00% w/w sodium fluoride. The ratio of cleaning fluid to internal tube area was approximately the same as in the sugar factories. The pH of the starting solution was 12.11. The piece of tube was totally clean after boiling for 2 hours at atmospheric pressure. The scale quantity removed was 61.34 grams per square foot and the final pH was 6.06.

Example 8

[00036] The composition of the cleaning solution was 3.0% Chelate A, 2.0% NaOH (solid), 2.0% NaF (solid) and 5.0% sodium acid sulfate. The tube section had an internal surface area of 5.007 square inches. The tube was clean in one hour and 15 minutes of boiling time. The final pH was 10.47 and the scale removed was 46 g/sq.ft.

What is claimed is:

1. A method for the removal of scale from equipment on which scale has accumulated which comprises treating the equipment surfaces having scale with a solution having a scale-removing effective amount of a sodium salt of a polycarboxylic acid chelating agent.
2. The method of claim 1 wherein the chelating agent is tetrasodium ethylenediaminetetraacetic acid or pentasodium diethylenetriamine-pentaacetic acid.
3. The method of claim 2 wherein the chelating agent is tetrasodium ethylenediaminetetraacetic acid.
4. The method of claim 1 wherein the scale contains at least one component selected from the group of calcium phosphate, calcium carbonate, silicic acid, calcium silicates, calcium oxalates, iron and aluminum silicates, calcium oxalate, calcium- or silica-containing minerals, proteins, amino acids, waxes and lipids, cellulose and hemi-cellulose.
5. The method of claim 1 wherein the concentration of the chelating agent is from about 3 to about 100 g/L.
6. The method of claim 5 wherein the concentration of the chelating agent is from about 25 to about 75 g/L.
7. The method of claim 6 wherein the concentration of the chelating agent is from about 55 to about 70 g/L.

8. The method of claim 1 wherein the pH of the chelate solution is about 7 to about 12.
9. The method of claim 9 wherein the pH is from about 9.0-10.0.
10. The method of claim 8 wherein sodium hydroxide is added to maintain the pH.
11. The method of claim 1 wherein the temperature of the solution during the scale-removing process is from about 20°C to about 120°C.
12. The method of claim 11 wherein the temperature is from about 50°C to about 110°C.
13. The method of claim 12 wherein the temperature is about 100°C to about 102°C.
14. The method of claim 1 wherein the chelating agent is tetrasodium ethylenediaminetetraacetic acid having a concentration of from about 55 to about 70 g/L.
15. A method for the removal of hard-to-remove scale from an evaporator apparatus which comprises treating the evaporator surfaces having scale with a solution having a scale-removing effective amount of a combination of a sodium salt of a polycarboxylic acid chelating agent, caustic and at least one of an additional compound effective in removing hard scale.

16. The method of claim 15 wherein the chelating agent is tetrasodium ethylenediaminetetraacetic acid or pentasodium diethylenetriamine-pentaacetic acid.
17. The method of claim 16 wherein the chelating agent is tetrasodium ethylenediaminetetraacetic acid.
18. The method of claim 17 wherein the additional compound effective in removing scale is selected from the group consisting of a fluoride, gluconic acid or sodium acid sulfate.
19. The method of claim 18 wherein the fluoride is selected from the group of ammonium bifluoride and sodium fluoride.
20. The method of claim 19 wherein the fluoride is sodium fluoride.
21. The method of claim 15 wherein the caustic is sodium hydroxide.